An SCC Initiation Model: Effects of Cold-Work in Austenitic Stainless Steels in Light Water Reactor Environment

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Abstract- **The growing recognition of cold-work as an accelerant in stress corrosion cracking (SCC) is well justified because of its common or persistent impact as a key factor in both the initiation and crack growth regimes. This recognition is also a result of the presence of cold-work often noted in the initial failures of several service components. The presence of cold-work limited to surface layer has been often attributed to the relatively early intiation of SCC. A component with bulk or volumetric cold-work condition resulting from mechanical or weld-related fabrication is also subject to a relatively higher growth rate due to SCC. In addition to the accelearating effects on SCC the cold-work increases the material strength and the sequence of fabrication can significantly affect the residual stress often related to the material strength as well. Therefore, the impact of cold-work on the SCC degradation and useful remaining life of such components needs to be assessed with some technical basis and a quantitative framework that account for the various influences of the cold-work.**

The above aspects are reviewed in this paper focusing on the non-precipitation-hardening stainless steels subject to the reactor water environments. Also, the related field observations and their significance in assessing the cold-work impact are discussed. It is shown that the residual stress including the strain-path and stress state, as well as the material condition seem to dominate the operating influence of cold-work on SCC. These factors are explicitly related to the SCC susceptibility in a quantitative framework discussed in this paper. The basis for inter-relation between the cold-work effects and SCC is presented in relation to the model parameters. Additional factors pertinent to the austenitic steels include their susceptibility to sensitization and phase transformation, particularly interacting with the presence and sequence of cold-work. Observations from the surveyed literature on these aspects are also discussed in relation to the proposed model.

Keywords- Stress Corrosion; Cold-Work; Initiation Model; Austenitic Stainless Steel; Stored Energy; Yield Strength

I. INTRODUCTION

It has been known for a long time that cold-work (CW) affects the stress corrosion cracking (SCC) performance of most metallic materials. The CW impact, which can promote or mitigate the SCC, cuts across most practical applications and alloys typically found in nuclear reactor systems as well [1–3]. Also, it is generally recognized that the adverse impact of CW in SCC is common or persistent in both the initiation and crack growth phases. More significantly, this accelerating effect is clear from several service related failures, and its assessment becomes a potentially critical issue for extended service well beyond 40 or 60 years. Both the surface layer limited cold-work and the through-thickness condition need to be assessed for their impact on the remaining useful life of many components. This includes mechanically-strained conditions due to weld-shrinkage and cold-bent elbows or similar geometries which result in volumetric effects of cold-working, as well as grinding. As such, the control of fabrication, weld-repair, and mitigation strategies need to address the cold-work factor, preferably with some basis and quantitative approach. This paper deals with the analytical and physical (mechanistic) aspects of a proposed framework for assessing the impact of CW on SCC response of normally ductile, solution-strengthening type alloys in aqueous environments.

The nature of the role that CW plays in SCC can be illustrated by the “three-ring” Venn diagram, Fig. 1, often used to describe the SCC itself. The similarity is striking but more significant is the fact that CW has a direct influence on all three areas needed or responsible in the manifestation of SCC. That is, CW affects a myriad of physical properties such as residual stresses, deformation response, microstructure, strength, and oxidation–corrosion. This mixed or complex role of CW in SCC was also thought to be responsible [4] for oft-quoted apparently confounding nature [5, 6] or lack of treatment [2] of this important factor in quantifying SCC – i.e., because the term cold-work, even if treated as a single variable, has multitude of effects, not all in one direction, on the SCC susceptibility. As a result, it is clear that there is no single quantity (or parameter) that can be labelled as THE cold-work factor for SCC susceptibility. Indeed, the recently presented model [7, 8] conforms to this notion and, even in its simplified form, identifies three factors somewhat parallel to these varied influences of CW.

Thus it was proposed [4, 7, 8] that a useful quantification of SCC should take into account the impact of CW on (a) the effective stress, (b) the local corrosion–deformation interaction, and (c) the micro-cracking tendency or propensity believed to be significant. Each of these influences on SCC susceptibility, or time-to-initiation of a short crack, was shown to be incorporated in three primary parameters of the model (discussed in the subsequent section), namely: a stress severity parameter (S/S_y), SCC-CW resistance factor (a_n), and a micro-cracking

resistance parameter (A). Also, a useful measure of cold-work was introduced and correlated with simple material strength properties and the strain-hardening behavior. The measure of cold-work was used in defining the relative SCC-CW resistance. The micro-cracking resistance parameter was shown to correlate well with strength properties. The stress severity parameter reflects residual and applied stress relative to the cold-worked yield strength. As a result, the quantitative framework demonstrated that there is no single (multiplicative or additive) factor that can capture the impact of cold-work on SCC and that the key effects can be characterized with good correlation to the likely physical manifestations of the CW.

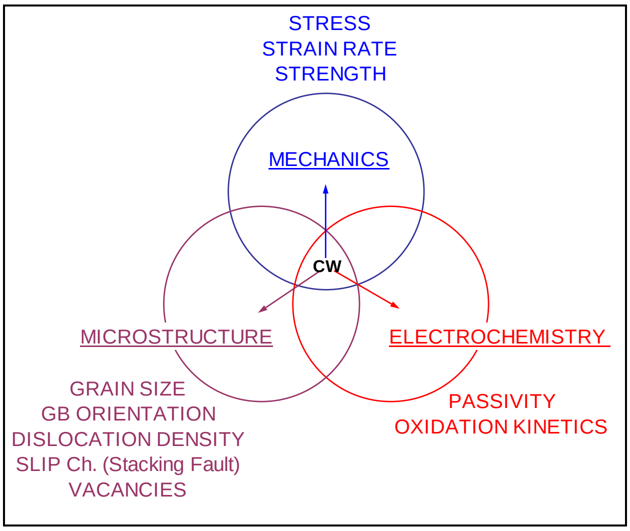

Fig. 1 Schematic of multiple physical effects of cold-work on SCC factors [4]

The above model is summarized in this paper in the context of its application to the SCC response of austenitic stainless steels in light water reactor environment. A brief update of a review of the related observations [7] from in-service instances and laboratory tests is included demonstrating the need and utility of this modeling work. The initial model development was based on similar data for the CW effect in SCC of Ni-Cr-Fe Alloy 600 in high purity or pressurized water reactor (PWR) primary water environment [8]. Work presented here demonstrates that the same framework has the potential to quantify the dependence of SCC on CW in the austenitic stainless steels. Results of model application are presented with a discussion of the underlying common processes and certain aspects more relevant to the stainless steels [7].

II. REVIEW OF FIELD AND LABORATORY OBSERVATIONS

The following brief review is to illustrate the significance of cold work as a contributing factor to SCC across varied environmental conditions/applications in light water reactors, particularly for the solute-strengthening type austenitic stainless steels which cover a vast area of the reactor coolant system pressure boundary. Since the early days of SCC observations in boiling water reactor (BWR) applications [9], it is generally well accepted that CW acts as an accelerant for SCC initiation and growth in the oxidizing or high potential aqueous environment, even in non-sensitized steels.

While the austenitic stainless steels in reactor coolant system service have shown much greater resistance to SCC in PWR environments compared with BWR, there have been some instances of intergranular stress corrosion cracking (IGSCC) in both the primary [3] and the secondary systems of the PWRs [10]. These instances have been generally shown to involve possible oxidizing conditions or contaminants in an otherwise reducing environment. However, high stress and/or cold-worked microstructure appear as common factors in these cases, whether or not high oxygen or contaminants are present or involved. The survey [3] showed that 17% of the events in the primary side in normal PWR water were attributed to heavy CW only (with reported hardness generally above 300 Hv); while the remainder 83% events were associated with oxygen, and presence of chloride or sulfate contamination, in addition to CW, where the impact of CW could not be decoupled from the water chemistry influence.

For example, IGSCC of a cold-worked bolt head of (non-stabilized) Type-316L steel was observed (after about 10 years operation) in the steam separator region of a PWR steam generator [10], while Ti-stabilized Type-316 without CW did not show such cracking. However, the local (crevice) condition was considered to be oxidizing. The Ti-stabilized Type-316 did show IGSCC at another location—PWR internals core barrel bolts—in the cold-worked microstructure within the high stress region of the bolt head, although the possible role of contaminants was not ruled out in these instances. Previously, Daret, et al. [11] reported that many cases of SCC in austenitic steels in the PWR primary circuit were observed (pre-1994) and attributed to excessive CW or irradiation related hardening, often with cyclic loads.

Service failures where CW itself plays a critical damaging role include both BWR and PWR austenitic stainless steel components. For example, some of the IGSCC initiation in PWR pressurizer heaters has been attributed to the CW condition of 304L stainless steel [12], with R&D results showing no crack growth below Vickers hardness of about 310 [13]. In BWR, for instance, even for the low-carbon or stabilized steel condition (i.e., very minimal sensitization) the occurrence of IGSCC in the reactor core shroud has been attributed to the effect of CW [14]. Couvant, et al. [15] reported prior IGSCC in the PWR pressurizer heater tubes of 316L grade stainless steel observing that the few cases coincided with high CW and stress fluctuations or strain localization.

Examples of the accelerating effect of CW on SCC of austenitic steels in BWR and PWR type environments tested in laboratories are numerous. Kaneshima, et al. [16] reported definite susceptibility and enhancement due to CW in the slow strain-rate tests in simulated PWR primary water environment in these steels. Crack growth acceleration due to CW even in unsensitized 304 and 316L in low corrosion potential (hydrogen water chemistry) range was reported in laboratory tests [17]. Guerre, et al. [18] showed measurable crack growth in cold-worked samples of Type 316L stainless steel in laboratory under PWSCC mode, provided the material was in a hardened state, suggesting the

importance of local mechanical properties in imparting the susceptibility. Takakura, et al. [19] reported IGSCC on irradiated cold-worked (12% & 20% strained) Type-316 stainless steel tested under constant load in simulated normal primary PWR water. Both the initiation time and the threshold stress level were found to decrease with increasing irradiation dose. These data also confirm the CW related susceptibility of stainless steels in the typical reducing conditions of PWR coolant. Couvant, et al. [20, 21] have suggested that, based on their finite element analysis, the enhancement of stress concentrations on grain boundaries due to complex loading (strain) paths also offered support for increased SCC initiation in austenitic stainless steels under simulated primary water as observed in their laboratory tests, while CW was expected to enhance diffusion and consequently oxidation effects as well.

III. CW-SCC INITIATION MODEL

In this work the term "initiation" is used in the engineering sense to denote the development of a singly dominating crack of engineering significance. From the model development and application point of view the definition of initiation can be made more explicit with the following considerations: (a) the implied depth is of the order of 0.4 mm to 2 mm, primarily depending on the part geometry: thickness and notch if present; (b) this range corresponds to an average crack growth rate uncertainty factor of about 2 which is reasonably low for the SCC phenomenon; (c) formulation validity is expected for other depths (down to a few grains) with simple, appropriate scaling of the model estimate; and (d) this definition is in the spirit of the well known Coffin-Manson rule for fatigue life and Section III of the ASME Boiler & Pressure Vessel Code. With these explicit considerations, it is expected that the term "initiation" is not as limiting or nebulous as might appear at first, and its validity and practical significance remain high, especially in dealing with the occurrence of SCC starting with a practically smooth or nominally defect-free as-built component condition.

A. *Cold Work Measure*

A new measure of cold-work, m, is introduced to enable quantification of CW-SCC effect capturing the primary influence applicable to, or described by, different ways of introducing and labelling the "cold work" in general. It takes into account changes in the yield and tensile strength as a function of cold work, reflecting the strain-hardening influence [8]. It is defined by the relation[1]:

$$m = f(S_y, S_u, n) = k \bullet (S_y/E)^a \bullet (r-1)^b \bullet (r)^c \qquad (1)$$

where,

r = strength ratio = S_u/S_y;

S_u= ultimate tensile strength[2];

S_y = tensile yield strength.

Here E is the Young's modulus of elasticity, ($a > 0$, $b < 0$, and $c < 0$) are empirical parameters, and n represents the material work-hardening. Note that the strength ratio, r, is greater than one, and it decreases with increasing cold work level. The parameter k is used as a normalizing constant to represent the initially un-deformed, fully annealed condition; and the lowest value for m is taken equal to one. Although the modulus of elasticity is used here mainly for non-dimensional purposes, the ratio (S_y/E) represents an average elastic strain at yield and $S_y(S_y/E)$ can be viewed to represent (twice) the elastic strain energy at yield. The ($r-1$) term relates primarily to the work-hardening response. The choice of using strength properties in the above relation was primarily for engineering reason that these properties are more readily available or estimated in a given application.

B. *Simplified Model*

The simplified model for time to initiation of a small crack, t_i, is then expressed as:

$$t_i = f(S, T, pH, \ldots) = a_n \bullet \lambda_e \bullet \ln\,[A/(S/S_y)] \qquad (2)$$

where,

a_n= (normalized) SCC cold-work resistance factor, primarily material (alloy) dependent;

λ_e= material/environment factor including the Arrhenius dependence on temperature, T

A = material/stress (or micro-cracking) resistance parameter of the model;

S = effective tensile stress, including residual stress

S/S_y = stress severity.

It should be noted that the three major parameters of the model are labelled to reflect their expected primary influence on the SCC response, namely: the stress severity parameter (S/S_y), the SCC-CW resistance factor (a_n), and the micro-cracking resistance parameter (A). These are not necessarily independent, in that, they are all influenced by the cold-work. Also, the combination of a_n and λ_e relates mainly to the effective interaction of the local deformation and environment, where λ_e accounts for the non-cold-work related environmental variables such as the solution pH, conductivity, corrosion potential, and temperature.

C. *Low-Stress Response Modification*

The form of SCC initiation function itself, Eq. (2), was derived from the results of strain-rate damage model (SRDM) [22] that has a more fundamental basis in that it relates SCC damage evolution to the interaction between the local electrochemical conditions and the material

[1] In the following description, all modeling relations are first expressed in a general form, using $f(\,)$ for the generic dependence, followed by a specific expression used in this work.

[2] Note that the values of material strength (S_y and S_u) used throughout this work as correlating parameters are for the actual, in-situ condition (i.e., either un-deformed, or cold-worked, or heat-treated, as the case may be) at normal room temperature. The choice of room temperature is for convenience of analysis and application, as the applicable high temperature strengths are often not determined or not readily available. Since these are generally well correlated, the choice is considered to be without loss of generality if the consistency is maintained in data assessment, model parameter determination, and model application.

deformation (strain-rate). This required the explicit use of a material constitutive relation and so the SRDM results were obtained for stress levels not much below the material yield strength. Therefore, Eq. (2) was not expected to be applicable well below the yield stress level. Also, there is a general expectation that near some very low stress the initiation time can rapidly increase to a very large value. These issues were addressed by the following modification of Eq. (2):

$$t_i = a_n \cdot \lambda_e \cdot ln\,[A] \cdot ln\,[(A-z)/(S/S_y-z)]\,/\,ln\,[(A-z)/(1-z)] \qquad (3)$$

where

$z = S_{th}/S_y$: threshold stress model parameter;

S_{th}= threshold stress estimate.

Note that for z=0, the above t_i is identical to the initiation function of Eq. (2). Clearly, the expected lack of data for very low stress severity values makes the use of engineering judgment necessary in determining this threshold stress factor (z), although the above provided an adequate modeling structure for this purpose.

The above formulation fully describes, and is referred to in the following, as the CW-SCC initiation model. SCC under the minimal or non-cold work condition is a particular case of this model. From the point of view of generating useful information about the model parameters the case of stress-severity equal to one should be of particular interest.

As noted earlier, for a given material–environment combination, all factors (a_n, A, z, and S/S_y) except λ_e, are affected by the level of cold work. This empirical observation was used to examine further correlations for these factors in terms of the strength properties as affected by the cold work. This examination was done for the case of Alloy 600 SCC in simulated primary water and high-purity water [8] which resulted in the following correlations as useful estimators for the three factors (a_n, A, z).

For a_n, the following simple power-law relation was found to correlate well with the Alloy 600 SCC data: $a_n = f(m) = a_1/m^q$, where q is an empirical parameter of the model. The normalized value of 1 for a_n may be taken to represent an initially un-deformed, fully annealed condition, so that for m=1, a_1 in the above relation is also 1. The overall dependence can be obtained from time-to-initiation data at various cold-work levels. Therefore, without loss of generality, a_n is taken equal to $1/m^q$ in this work.

An earlier evaluation of SRDM response [22] suggested that the factor "A" was likely to be less dependent on temperature and environmental conditions, and its variation was likely to be dependent on strength properties. The evaluation of above CW-SCC model versus the SCC data on Alloy 600 [8] showed a strong correlation between "A" and the strength ratio "r", suggesting an exponential dependence to be adequate. The same evaluation also suggested a simple logarithmic correlation between the stress threshold factor, z, and the strength ratio. In summary, the following correlations were found to be suitable to represent the SCC data on Alloy 600 with the above CW-SCC initiation model:

$a_n = 1/m^q$

$A = v \cdot exp\,[w \cdot r]$

$z = z_1 + z_2 \cdot ln\,[r]$

where, q, v, w, z_1, and z_2 are empirical parameters. Note that all the model factors or parameters are non-dimensional, except for λ_e that has the dimension of time.

IV. DATA AND MODEL RESULTS

A. *Test Conditions and Data*

The application of above CW-SCC model for the observed SCC response under cold-work condition of an austenitic type stainless steel is demonstrated here with the use of data reported by Pickett and Sim [23]. It was one of the earliest comprehensive studies undertaken to determine the effects of applied stress and cold-work on IGSCC of sensitized and non-sensitized Type-304 stainless steel in the simulated BWR coolant with 0.2 ppm dissolved oxygen. The water was circulated through test vessels (made of Type-347 stainless steel) and maintained at 282°C, with conductivity of 1.5 to 3.0 µS/cm and chloride content of about 0.5 ppm. The test vessels allowed multiple specimens to be tested under constant load—the system recently described as the "Keno" autoclave loading machine [24]. The time-to-failure for each specimen was indicated by matching surges in pressure recordings.

The test specimens were made from 5/8-inch plate of Type-304 stainless steel with chemical composition of (% wt): C (0.057), Mn (1.57), N (0.08), Cr (18.8), Ni (8.9), Si (0.42), Mo (0.43), Cu (0.22), P (0.029), and S (0.016). The plate was solution-annealed at 1065°C (ASTM grain size number 3.5). The specimens were machined after cold-rolling the plates to 5%, 8%, and 20% thickness reductions. Some specimens were heat treated for sensitization at 621°C for 24 hours, followed by furnace cooling. Note that all non-sensitized samples, with any level of cold-work, survived the 10,000-hour test period limit used to stop further exposure. Therefore, the following analysis and results deal primarily with the sensitized material condition used in the above tests.

Table 1 summarizes the SCC test conditions which covered up to four stress levels for each of the four cold-work conditions described above. Three specimens were tested for each combination of the cold-work and applied initial stress. The observed time-to-failure values are listed, with 10,000 hours or a "+" symbol in Table 1 indicating the maximum test duration (run-off).

Data from their mechanical (non-SCC) tensile tests were used here to estimate the room temperature yield and ultimate strength values for the sensitized material condition. For the 0, 5, 8, and 20% cold-work conditions the estimated yield strengths were 274, 403, 449, and 601 MPa, respectively; and the ultimate strengths were 631, 669, 689, and 793 MPa, respectively. The resulting stress severities estimated for various tests are listed for reference in the additional column of S/S_y in Table 1.

TABLE I TEST PARAMETERS AND FAILURE TIMES FROM THE CONSTANT LOAD TESTING OF SENSITIZED TYPE 304 STAINLESS STEEL IN SIMULATED BWR WATER [23] (SEE TEXT FOR ADDITIONAL DETAILS)

CW (%)	S (MPa)	S/Sy	Tf1 (hrs)	Tf2 (hrs)	Tf3 (hrs)
0	153.1	0.558	7000+	10000+	10000+
0	193.1	0.704	9608	10000+	10000+
0	248.2	0.905	794	1913	2936
0	302.7	1.104	296	1518	2011
5	248.2	0.616	2769	4125	10000+
5	302.7	0.751	1590	1696	1746
5	386.1	0.958	291	582	1068
8	302.7	0.673	8600+	9927	10000+
8	386.1	0.859	767	1032	1642
8	475.7	1.058	486	648	815
20	475.7	0.792	1217	1812	3335
20	577.1	0.961	602	631	1969

B. Model Parameters

Since one of the goals of this work was to assess the validity or extension of the same basic model (from the Alloy 600 work [8]) to the case of IGSCC in austenitic steels, it was thought essential to keep the model the same except for the values of model parameters. Compared to the multiple and wider sets of data available for the Alloy 600 IGSCC used in developing the described model, the above single set is limited to one heat of material and one source of data. Therefore, the effective approach here was to use the Alloy 600 model parameters as a guide, keeping any deviations to a minimum, and perform a constrained optimization to best fit all of the data given in Table 1 in determining the new model parameters for the case of stainless steel in the test environment.

The annealed material condition of Type 304 stainless steel was represented with E = 206,000 MPa and k = 10 based on a review of the expected range of mechanical properties for the stainless steel application. The likely variation of modulus of elasticity with cold work is assumed to be negligible in this work. The values for empirical parameters (a, b, and c) to quantify the cold-work measure (m) were 0.25, –0.75, and –0.25, respectively, as used in the case of Alloy 600 based on an engineering judgment concerning the material strain-hardening response. The optimization process resulted in the following values for the model parameters, using the same correlating functions described above for Alloy 600, by effectively minimizing the deviation of log-mean life between the overall model and the data: $q = 0.175$, $v = 0.9$, $w = 0.166$, $z_1 = 0.4$, and $z_2 = 0.16$; also, the resulting non-cold-work-related factor λ_e for the environmental conditions of this data set was estimated to be 257 days. With these parameters the model estimates for time-to-failure were determined for all tests of Table 1 and the results are described below.

C. Model Results vs. Data

As noted above, the CW-SCC model includes the case of non-cold work condition as a particular case; therefore it is of interest to compare the model response with data for this condition. This comparison is shown in Fig. 2 where the stress severity dependence of the mean-log time-to-failure data for samples with zero imposed cold-work is compared with the model estimates. Note that the model curve in Fig. 2 is not a best-fit to the data points shown; it is the estimate obtained from the overall optimized model based on all of the data including those at other cold work and stress levels (in Table 1). As such, the good fit exhibited in Fig. 2 confirms at least the internal consistency of the derived model, and that the model response is in good agreement with the overall stress severity dependence over the range of SCC initiation life including the likely threshold region.

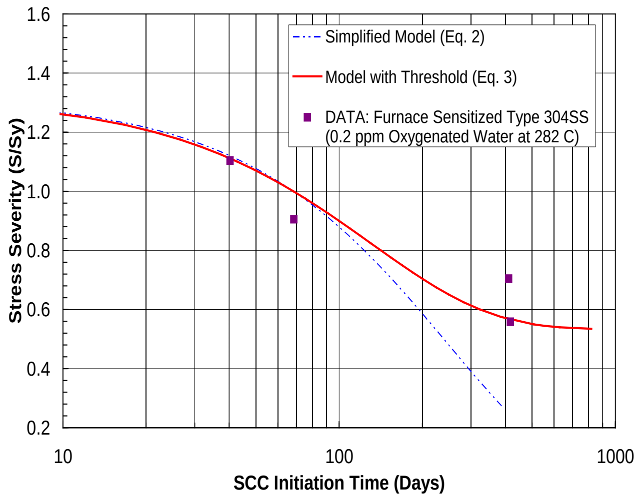

Fig. 2 Model comparison with data for IGSCC failure time under constant load tests of sensitized Type 304 stainless steel in simulated BWR water, for non-cold-worked condition

The observed influence of stress under various levels of cold work is shown in Fig. 3, where the numerical label along each bar indicates the stress severity imposed under each of the tested CW condition. For this data set, the trend shows that for any specific CW condition the lower the stress severity the longer is initiation life. The model estimates are compared (solid symbols in Fig. 3) with the observed data medians and ranges under each of the tested CW conditions, which show the same trend with respect to the stress severity as well as the level of cold work in good agreement with the data. The scatter band on estimated life is shown in Fig. 4, comparing it with the scatter observed in these tests.

This comparison shows most data are within about a factor of two on the model estimated life. Note that the factor of two is on the life; this factor for SCC (as in fatigue life) is well within the expected variability that is in general several times greater for the crack initiation time (as for the crack growth kinetics). The systematic trend in data scatter (i.e., from low to high sets in observed life) relative to the perfect prediction line (Fig. 4) shows a reasonable confirmation of the goodness-of-fit of the model, given the limited number of tests and the expected variability in material properties and in the SCC kinetics.

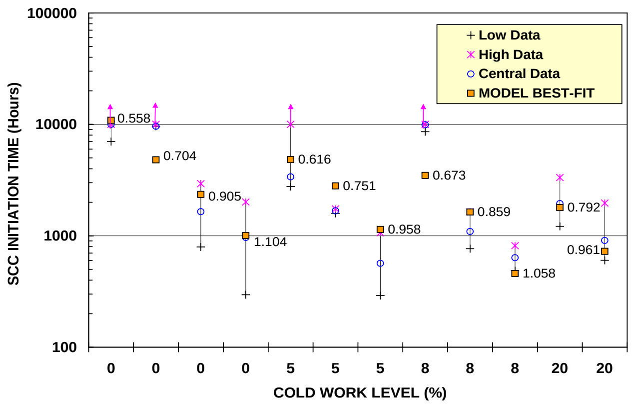

Fig. 3 Model comparison with data for IGSCC failure time under constant load tests of sensitized Type 304 stainless steel in simulated BWR water, for various cold-work conditions

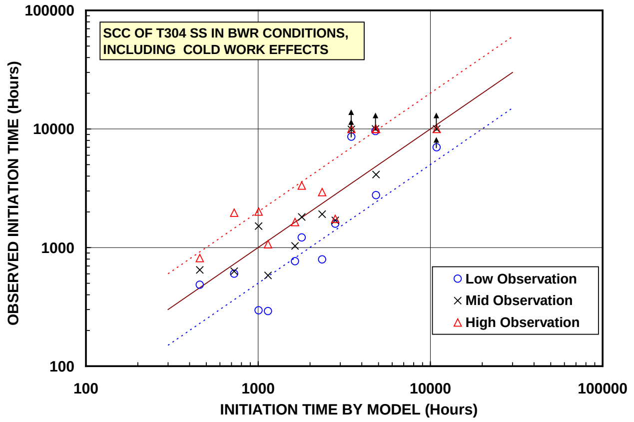

Fig. 4 Goodness-of-fit for CW-SCC initiation life model in comparison with data and observed scatter

V. DISCUSSION

As noted earlier, the modeling framework recognizes that cold work is a process that affects many material factors with varied influences on the SCC response, and cannot be adequately represented as a single model factor (or parameter) in defining a quantitative relation between its impact on the material and its SCC susceptibility. Thus, there are three main factors in the susceptibility model, Eq. 3, which are affected by the cold work: A, a_n, and S/S_y, in addition to the threshold stress parameter, z. These in turn have been correlated or expressed in terms of the strain-hardened material properties, mainly the yield and ultimate strengths. These properties represent the limiting states of the material deformation response. For a given material or an alloy, there is a strong correlation between these properties and the percent elongation as well as the material strain hardening. Therefore, to a first approximation, no need is indicated in the current work to add more explicit consideration other than the use of two strength properties. One more model factor, λ_e, defines the material–environment influence on SCC susceptibility to account for variables of temperature, pH, etc., independent of cold work.

The emphasis in this work on the strength (strain hardening) properties and microstructural character is a natural consequence of their significance in the CW-SCC interaction. This significance is expanded upon first in the following discussion [4, 7], providing a basis for such a choice. This is followed by a brief discussion of sensitization, stacking fault energy (SFE), orientation effects, etc. and their assessment in CW-SCC modeling framework presented above. It is also useful to note that, in addition to being the limiting states for the material deformation, the yield and ultimate strengths are well defined as material properties, unlike hardness.

A. *CW, Defects, and Oxidation*

The immediate manifestation of cold working a metal piece is the introduction of microstructural deformation and thus defects and consequential microstructural changes. These include elongation of grains (accompanied by an increase in grain boundary surface per unit volume), re-orientation of grains (texture) relative to the direction of working, increase in dislocation density and sub-structures, increase in sub-grains (or "blocks"), vacancies, etc. What is important to note here is that it is the interaction with these cold-work induced defects and microstructural changes that influences the character and kinetics of the basic processes responsible for SCC: namely the deformation response and the (grain boundary) passivation response, notwithstanding the diffusion and adsorption within the grain boundary structures. The resulting greater strain localization and increased strength both are expected to contribute to the increase in SCC susceptibility whether film rupture or hydrogen interaction is involved.

Increased number of vacancies is likely to enhance the CW effect on SCC. For example, especially under the tensile stress, vacancy migration and accumulation preferentially in the direction of tensile stress at interfaces across which the tensile stress is acting can increase the propensity to interface separation (and/or diffusion of species involved in the SCC). This effect will be even more pronounced at higher temperature and lower strain rate [25] known to accelerate SCC.

Effect of cold-work on the passivation response of Type 304 stainless steel in sulfate media was recently examined by Barbucci, et al. [26] with the observation that "The higher passive currents and increased susceptibility… explained by the formation of much more defective oxide… related to the formation of defects in the grains and of more defective interfaces… both resulting from the accumulation of internal stresses due to cold-rolling." Other studies have also shown that the CW has more pronounced (detrimental) effect in the passive region than in the peak active polarization region. Also, it is interesting to note a recent observation of some selective (internal) oxidation taking place in the proximity of a crack front – where protruding finger-like oxides were determined to be present along certain slip planes (intersecting the grain boundaries) [27]. This was for a sensitized condition with cold worked sample of 304 stainless steel exposed to hydrogenated high-purity water (reducing condition)–indicative of the possible role of defective/susceptible interfaces enhancing the diffusion process due to cold work.

B. CW, Stored Energy, & Strength

Also it is significant to note that a small but measurable part of the energy of cold working a material is retained within the resulting microstructure well after the working is finished. This is often referred to as the stored energy, and it is also a reflection, or a measure, of the above noted defects/interfaces generation. This energy must play a role in the local deformation and fracture response, especially as a driving force for certain mechanism(s), since when facilitated (by the mechanism) the stored energy is released (i.e., it is made available to aid the mechanism lowering the system energy, thereby reducing the work required for producing new interface area). Note that any attempt to relate the overall increase in stored energy, even if accurately measured, either to the thermodynamic quantities or directly to the SCC susceptibility itself will remain inadequate. This is mainly due to the fact that it is the local (spatial) distribution of the stored energy that is expected to play the significant role in relation to SCC, more so than the overall increase (e.g., it cannot be estimated simply from the raised electrochemical potential based on an average value). The stored energy is also expected to help maintain the crack-tip sharpening, in part by providing an immediate local source of free energy, with associated increase in strain hardening and reduction in micro-fracture toughness enhancing the local micro-cracking tendency over plasticity. These effects of CW are significant contributors to the resulting increase in SCC susceptibility. While the stored energy of CW is difficult to measure or quantify it also has been correlated with the increased level of flow strength.

In the above context it is important to note the closer connection of the strength properties, rather than the straining level, of the cold-work and the microstructural changes of SCC-significance. This is best exemplified by the work of Taylor and Quinney [28] leading to their conclusion: "The fact that the absorption of latent energy and increase in strength both cease when the same amount of cold work has been applied suggests that the strength of pure metals may depend only on the amount of cold work which is latent in them. Additional significance of their critical experimental work is that it showed the importance of increased strength, as a measure of the stored of energy, to be the factor to represent cold-work more so than the level of plastic strain itself. That is, as they demonstrated by comparing torsion versus tension pre-straining, large plastic strain (in torsion) could be realized without the attendant (further) increase in the actual cold-work character of the material, concomitant with the peak in the strength level.

It follows from the above assessment that, to a first approximation and for engineering purposes, it is sufficient to use the material strength and strain-hardening parameters as the key variables to quantitatively relate the level of CW to SCC susceptibility. This is notwithstanding possible deformation mode differences, as in the case of irradiation hardening, which may be more directly related to the other model parameters. It also implies that the material constitutive relation is incorporated more directly into the assessment. This is the basis used in developing the above SCC susceptibility model to quantify the role of cold-work.

C. CW, Sensitization, and SFE

It is well known that material sensitization (Cr-depletion near grain boundaries) is a significant factor in the IGSCC of austenitic stainless steels. This may require additional consideration when assessing the role of cold work, especially with regard to the fabrication sequence. One reason for expecting some sequence effect is that in the case of sensitizing treatment after cold work, especially high level of cold work, the microstructure will provide more carbide precipitation sites throughout the matrix along with higher diffusivity due to the dislocations and vacancy distributions. That is, for highly cold worked material the effect of (subsequent) grain boundary sensitization (on adjacent Cr-depletion) will likely be less severe. At the same time, some recovery of the micro-stresses from heavy cold-work will contribute to a reduction of the SCC susceptibility depending on parameters of the sensitization treatment. It also implies that not considering this effect may lead to potentially misleading comparison between SCC resistance of sensitized non-cold-worked condition and sensitized cold-worked condition. For similar reasons, it is likely that the beneficial effect of a deliberate cold-work process may be not as much in Type 304L as in Type 304 stainless steel. Although not discussed here in detail, the interactive effects of martensitic structures, cold work, and sensitization may add to complication in the assessment (e.g., [29]). It seems important to perform critical tests and establish relative significance of these effects by comparing sensitivity to related model parameters. Currently there is need for more data that would enable further assessment of these interactive effects in the austenitic steels.

The stacking-fault energy (SFE) is another factor likely to be significant both in influencing the SCC response with CW and in model parameter correlation. This is primarily due to the expected influence of SFE on the character of dislocation structure and the resulting slip distribution, in turn affecting the local film rupture frequency as well as the repassivation response (e.g., [30]). In addition, it is thought that the micro-cracking tendency will be influenced by the SFE. These different influences are related primarily to two separate parameters of the model (A and a_n). Again, not all such differing influences are expected to be in one direction or independent of other factors, but strain localization and strain-hardening seem important here as well (e.g., [31]).

D. Additional Comments

It is interesting to note that a recent assessment of SCC [32] supports the basis that the yield strength (increase due to CW) has a dominating influence in the SCC occurrence and kinetics, for Ni-base and the austenitic stainless steels. Thus, it would appear that, while there are several contributory or correlating factors (sensitization, SFE, etc.) still to be quantitatively well understood in the case of typical austenitic steels, perhaps the net predominant effect of cold work on SCC is well represented by the mechanical (strain hardening) properties and that the adopted modeling framework is a good start for its further application development. Also, the three parameters (a, b, c) used in quantifying the cold-work (Eq. 1), while empirical in the

overall SCC initiation model described above, are meant to represent the state of microstructure resulting from the process of cold-work; i.e., in principle, these may depend on the type and processing of the cold-work which may not be fully captured by the strength properties alone – however, such dependence is considered to be of secondary influence, and are treated in this work as fixed for a given alloy.

The modeling described in this work did not explicitly address the anisotropy or directionality of properties due to CW, or the Bauschinger effect due to relative directionality between the cold work and applied loading. The described development considered that these effects are conservatively included in the manner in which the data and application inputs are generated or used. The underlying formulation and use of material strain-hardening characteristics (to quantify the cold work influence) remain the same, except that a more general (multi-axial) stress and strength model extension should be used to address these details.

The geometrically necessary changes (grain boundary angles, shortening of relatively higher resistance grain boundary surfaces, and lengthening of grain boundary paths of lowered resistance) as well as the orientation of higher energy boundaries (relative to the loading direction) all contribute to the increased susceptibility that is now subject to a greater variation after the cold working. The statistical nature of these combined variations should also result in the increased likelihood of wide variation in SCC susceptibility between the orientations. It is suggested that these aspects be further examined for integration in the predictive model.

VI. CONCLUSION

An engineering model was presented for assessing key influences of cold-work in SCC of austenitic stainless steels in light water reactor environments. The model incorporates a useful measure of cold work relating the material strength and strain hardening properties. This measure was related to the SCC susceptibility in a formulation derived previously from the strain-rate damage model. In particular, the interactive and inter-dependent influence of stress, strength, strain-hardening, and cold work on SCC was quantified. The model as described is the same as developed for the Ni-base Alloy 600 in PWR environment [8], but with parameters derived for the case of Type-304 stainless steel in a BWR type environment. Good quantitative agreement with data was shown for the dependency of SCC initiation in relation to both the degree of cold work and the applied stress. This model extension and its results are encouraging in considering its general applicability. One expected benefit of this work is the development of a simplified yet general engineering framework to help quantify the effects of cold work on ranking of material heats or components, and on the assessment of various mitigation techniques by taking into account their impact on the appropriate model factors influencing the SCC response.

Also, the role of cold work in SCC of austenitic stainless steels under reactor water conditions was reviewed with service performance and related laboratory observations demonstrating the need and utility of the presented modeling work from a practical perspective. A detailed justification for emphasizing the microstructural and strength properties in this modeling framework was presented in relation to the key mechanistic aspects of the varied influences cold work is likely to have on the underlying SCC factors or processes.

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